Step Bunching: Influence of Impurities and Solution Flow

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The Problem

Step bunching results in striations even at relatively early stages of development and in inclusions of mother liquor at the later stages. Therefore, eliminating step bunching is crucial for high crystal perfection. Step bunching is morphological instability which can be influenced by solution (or melt) flow,[1-4] impurities changing the step kinetics,[5] and by random nature of step generation and ridges on a growing surface.[6] Relative importance and interrelation between these mechanisms is not clear, both from experimental and theoretical standpoints. Addressing these issues, along with evaluation of instabilities at their later stage, is the major goal of the present project. In this work, the effects of supersaturation, impurities, and solution flow are addressed theoretically and experimentally.

Theory

Influence of supersaturation

A vicinal face possessing a constant slope p should lose its stability at lower face growth rates, V, and within smaller range of perturbation vectors, k_x, as the vicinal slope increases. We have calculated the stability region on the (k_x, V) plane for the case when the step rate, v, and vicinal slope linearly and non-linearly rises with relative supersaturation, s, while the face rate $V=pv$ rises correspondingly.[7]

At the p rising with supersaturation linearly (p=0.117s, as it follows from experiment), the stability region changes dramatically as compared to p=const. Namely the instability region starts at a definite growth rate and k_x and expands at higher rates (i.e., supersaturation). On the contrary, at p=const, the instability should occur at lower growth rates while self-stabilization effect is expected at high rates (supersaturations).

Influence of impurity

Impurity often results in a fast, superlinear rise of step kinetic coefficient with supersaturation, s, within a finite supersaturation range around some $s=s$ *, and is about linear otherwise. The corresponding $p(s)$ dependence, has a minimum at s_(s)* corresponding to the superlinear $v(s)$ with such. The present calculations show that such $v(s)$ and $p(s)$ dependencies new regions of instability at supersaturations close to s*. This result of calculations is consistent with experimental findings.[5] However, in experiment, the instability was reported at high flow shear rates while in calculations it should disappear above certain shear rates.

This contradiction might be an apparent one since no systematic experiments for different flow rates, step orientations with respect to the flow, and impurity induced non-linearity have been done so far.

Experiment

Stability of lysozyme bipyramidal square-shaped face, ~120 µm long, was analyzed under conditions of natural convection with expected flow rates, u =10 µm/s and forced flows at u=105 µm/s, 265 µm/s. Surface profiles fluctuations of normal growth rate and local vicinal slopes between was 3 test points, # 1, #2, and #3, were also measured interferometrically.[6,8,9] Fluctuations of normal growth rate in time were Fourier analyzed. The pair of points #1 and #2 was oriented along the flows, the pair #1 - #3 was normal to the flow. The steps were generated at or close to the crystal corner near the point #1. The profiles between #1 and #2 were: slightly concave at natural convection, convex at u=105 µm/s and slightly wavy with a shallow valley in the middle at u=265 µm/s. The temporal fluctuations were found to moderately rise from #1 to #2, but were practically equal for #1 and #3. This is in agreement with the flow induced or enhanced bunching effect. The fluctuations of v and p are essentially less in amplitude in both #1 and #2 test points at u=265 µm/s, as compared to u=105 µm/s.

Discussion and Conclusions

Existence of fluctuations corresponding to step bunches passing the test point #1, close to the step source, along with the ones in #2 and #3, suggests that the experimentally observed bunching might occur at the very beginning, during the step generation and is only enhanced in course of propagation along the face. Therefore the theory analyzing only onset of instability is insufficient to treat the data: evolution of bunches, along with their generation at the dislocation and/or nucleation sources is needed. Suppression of fluctuations by the faster solution flow may be associated with coupling of step generation rate by either dislocations or 2-D nucleation, both non-linearly dependent on supersaturation, with diffusion in the very vicinity of the generation area.

References

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